

# The Study on the Capacity of NO<sub>x</sub> Storage-Reduction Catalyst for Lean-Burn Engine

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**Abstract** Components in NO<sub>x</sub> storage reduction (NSR) catalysts have been studied in order to identify their impact on NSR performance. In order to enhance the catalytic performance of the NSR catalyst, the hydrothermal stability and sulfur tolerance of the NSR catalyst were improved by developing new NSR formula. The results show that Pt/BaO/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> + Rh/Al<sub>2</sub>O<sub>3</sub> catalyst has superior NSR activity, thermal stability and sulfur tolerance. The influence of space velocity, oxygen concentration and Lean-Rich period on the NSR activity was investigated.

**Keywords** Lean-burn engine · NO<sub>x</sub> storage reduction · Thermal stability · Sulfur tolerance

## 1 Introduction

Lean-burn engines are attracting more and more attention than conventional gasoline engines due to their higher fuel efficiency and lower CO<sub>2</sub> emission. However, under lean-burn conditions, the toxic NO<sub>x</sub> exhaust emissions cannot be efficiently reduced over the classical three-way catalysts in the presence of

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excessive  $O_2$ . Therefore, selective catalytic reduction (SCR) and  $NO_x$  storage-reduction (NSR) catalysts have been developed [1–3]. Because of their ability to achieve high  $NO_x$  conversions over a range of temperatures without the need for additional on-board reductant, and require less mounting space,  $NO_x$  Storage-Reduction (NSR) technology is regarded as the most practical technology for lean-burn gasoline and diesel vehicles. The development of advanced catalyst makes one of the major contributions to the improvement of NSR technology.

A typical NSR catalyst formulation contains  $NO_x$  storage components, noble metals and support oxides. The combined interactions of these three components efficiently remove  $NO_x$  from vehicle exhaust through the periodic operations of  $NO_x$  oxidation,  $NO_x$  sorption,  $NO_x$  release and  $NO_x$  reduction. Since the 1990s, NSR technology has been extensively studied, providing fundamental insights into the relevant reactions, mechanisms, kinetics, and roles of different catalytic components [4]. However, the role of every component in the NSR performance and the inter-component relationship are still not very clear. Meanwhile, the state-of-the-art NSR catalyst ( $Pt/BaO/Al_2O_3$ ) is weakly resistant to sulfur poisoning and thermal treatment. So it's necessary to develop the higher catalytic activity, thermal stability and sulphur tolerance NSR catalyst to meet the commercial requirements.

In this work, the influence of  $NO_x$  storage components, noble metals and support oxides on the catalytic activity was investigated. In this work, the influence of  $NO_x$  storage components, noble metals and support oxides on the catalytic activity was investigated. The influence of space velocity, oxygen concentration and Lean-Rich period on the NSR activity was investigated.

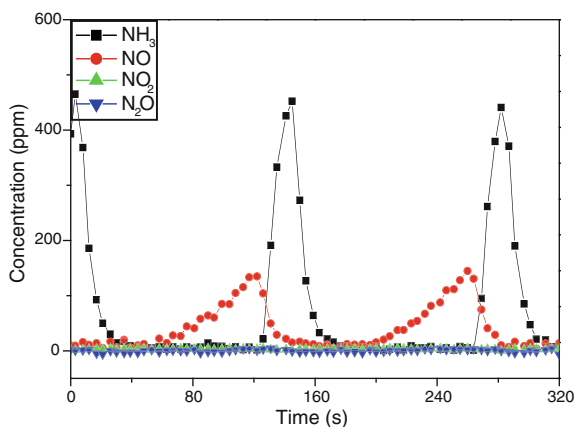
## 2 Experimental

$Al_2O_3$  supports (Shanghai Huaming Gona, designed as AC) are containing of 95.1 wt%  $Al_2O_3$  and 4.9 wt%  $La_2O_3$ .  $BaO/Al_2O_3$  was prepared as described by incipient-wetness impregnation of  $Al_2O_3$  using  $Ba(CH_3COO)_2$  solution. To clarify, the barium loading in all samples was denoted by the weight ratio of  $BaO$  to  $Al_2O_3$ , i.e.  $BaO/Al_2O_3(w/w)$ . After the impregnation, the sample was kept overnight at room temperature, and then the sample was dried at 120 °C for 12 h and then 500 °C for 3 h. For higher  $BaO$  loading ( $BaO/Al_2O_3 \geq 0.3$ ), successive impregnations were required. For  $Pt/BaO/Al_2O_3$  sample,  $Pt$  was loaded by incipient wetness impregnation, using  $Pt(NO_3)_2$  solutions. Then the sample was placed at room temperature overnight, dried at 120 °C for 2 h, and calcined at 500 °C for 3 h subsequently.

For  $Pt-Rh/BaO/Al_2O_3$  sample,  $Pt$  and  $Rh$  was loaded by a certain ratio, using  $Pt(NO_3)_2$  and  $Rh(NO_3)_3$  solutions.

For  $Pt/BaO/Ce_{0.7}Zr_{0.3}O_2+Rh/Al_2O_3$  sample,  $BaO$  were loaded on  $Ce_{0.7}Zr_{0.3}O_2$  support oxides by the incipient wetness impregnation.  $Pt$  and  $Rh$  were loaded respectively in  $BaO/Ce_{0.7}Zr_{0.3}O_2$  and  $Al_2O_3$  supports by incipient wetness

**Fig. 1** 120 s (lean)–20 s (rich) NSR reaction profiles of NH<sub>3</sub>, NO, NO<sub>2</sub>, and N<sub>2</sub>O



impregnation, and they were mixed in the weight ratio of 4:1 right before the catalytic tests.

The aging experiments were carried out in 5 % steam + air ( $SV = 30000 \text{ h}^{-1}$ ) at  $670^\circ\text{C}$  for 8 and 16 h, respectively.

The sulfur aging experiments were carried out in 8 % steam + 50 ppm  $\text{SO}_2$  + air ( $SV = 30000 \text{ h}^{-1}$ ) at  $300^\circ\text{C}$  for 24 h.

The NSR activity was determined under multipoint isothermal conditions in the temperature range of  $200\text{--}500^\circ\text{C}$  at an interval of  $100^\circ\text{C}$ . The alternative pulses of lean (500 ppm NO + 7.5 %  $\text{O}_2$  + 10 %  $\text{CO}_2$  + 10 %  $\text{H}_2\text{O}$ ) and rich (500 ppmNO + 7.5 % CO + 10 %  $\text{CO}_2$  + 10 %  $\text{H}_2\text{O}$ ) were injected under 120 s/20 s lean/rich cycles. The total flow rate is 1 L/min with the space velocity of  $30000 \text{ h}^{-1}$ . The outlet concentrations of NO, NO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O, CO, CO<sub>2</sub> and H<sub>2</sub>O(g) were measured by NICOLET is10 FTIR equipped with a 2 m gas cell (As shown in Fig. 1). The NO<sub>x</sub> conversion was calculated based on the following equations:

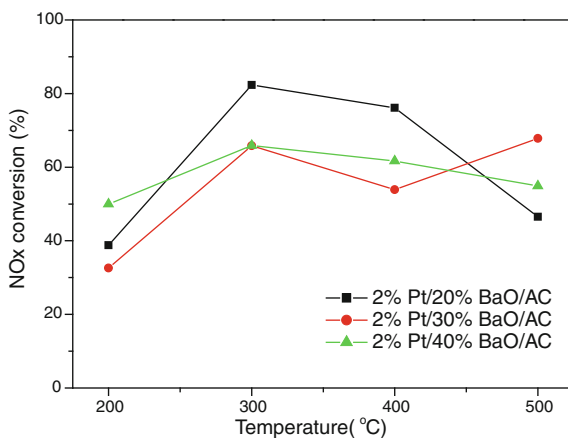
$$X_{\text{NO}_x} = \frac{\text{NO}_{\text{inlet}} - (\text{NO}_{\text{outlet}} + \text{NO}_{2\text{outlet}} + 2\text{N}_2\text{O}_{\text{outlet}})}{\text{NO}_{\text{inlet}}} \times 100 \%$$

### 3 Result and Discussion

#### 3.1 Influence of Storage Component

As a storage component, generally alkali metals or alkaline earth metal compounds are common in use because of their high basicity. BaO is the most commonly studied NO<sub>x</sub> trapping component among metal oxides, with a major contribution to the overall NO<sub>x</sub> trapping capacity. Besides the NO<sub>x</sub> storage step, BaO also plays some roles in the NO oxidation, NO<sub>x</sub> release and NO<sub>x</sub> reduction steps.

**Fig. 2** Influence of storage component loading on NSR activity

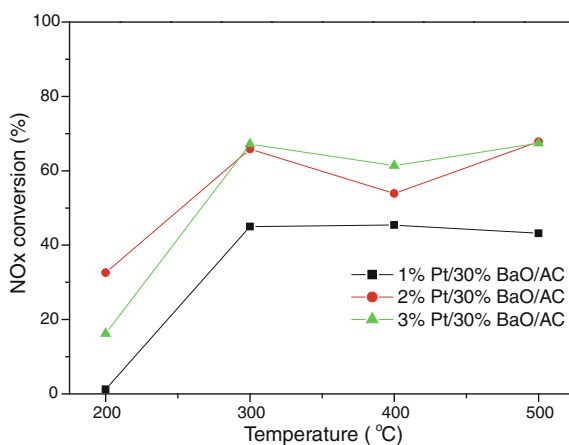
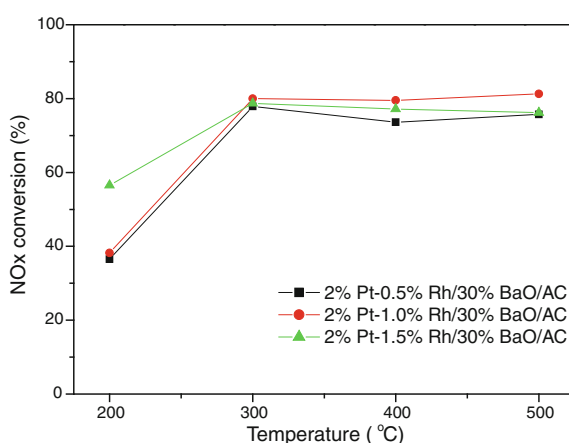


Perusal of the literature shows the distribution and dispersion of Ba-containing species and consequently the influence on the reactivity can be distinctly influenced by the Ba-loading [3, 5, 6]. According to Lietti et al., the relative amount of Ba-containing phases ( $\text{BaO}$ ,  $\text{Ba(OH)}_2$  and  $\text{BaCO}_3$ ) was different with different Ba loading, which has various  $\text{NO}_x$  trap capacity [7]. The results show that 20 % Ba loading was the optimum (Fig. 2).

### 3.2 Influence of Noble Metal

The noble metals (NM) plays several key roles in the  $\text{NO}_x$  storage/reduction reaction steps, such as (I) NO oxidation under lean-burn conditions(II)  $\text{NO}_x$  storage under lean-burn conditions (III)  $\text{NO}_x$  reduction under rich-burn conditions, and (IV) sulfur tolerance and regenerability. Detailed investigations have showed that NSR activity is relating to the noble metal dispersion, which is decided by particle size, precursor and loading etc [8]. The present investigation was to investigate the correlation between Pt loading and NSR activity. The results show that the increase of Pt loading resulted in superior NSR activity. However the higher loading resulted in its relatively higher cost. So the optimum Pt loading was 2 %.

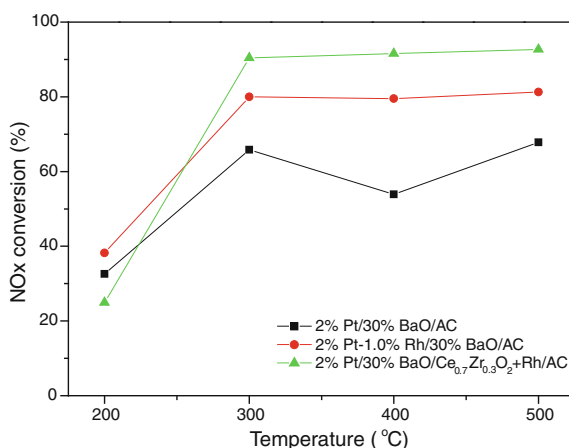
Generally, it has been reported that Pt shows higher NO oxidation activity than Rh and Pd, whereas Rh shows the highest  $\text{NO}_x$  reduction activity among Pt, Rh and Pd [5, 6, 9]. Therefore, it is very interesting to investigate Pt–Rh based bimetallic NSR catalysts to achieve a higher overall  $\text{NO}_x$  conversion. The bimetallic Pt/Rh samples were prepared with different Rh loading. The results show that the increase of Rh loading resulted in superior NSR activity, especially for low-temperature activity (Figs. 3 and 4).

**Fig. 3** Influence of noble metals loading on NSR activity**Fig. 4** Influence of noble metals on NSR activity

### 3.3 Influence of Support Oxides

The noble metals and the storage components are dispersed over a support; the support oxides is not only for dispersing NM and NO<sub>x</sub> storage components, but is of great importance for direct NO<sub>x</sub> trapping, N<sub>2</sub> selectivity modification, and sulfur tolerance improvement. Ceria-based materials have been shown to be beneficial for NSR catalysts [10]. Many current commercial samples have already incorporated ceria into NO<sub>x</sub> traps catalysts, although ceria-based materials are admitted to have several drawbacks. In comparison with pure CeO<sub>2</sub>, ceria-zirconia (CZ) solid solutions are well known for their improved redox activities and thermal stability. Therefore, it is of interest to apply CZ as support for NSR catalysts. According to Strobel et al., Pt/Ba/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts showed superior NSR performance, sulfur resistance and regeneration ability than Pt/Ba/Al<sub>2</sub>O<sub>3</sub>

**Fig. 5** Influence of support oxides on NSR activity



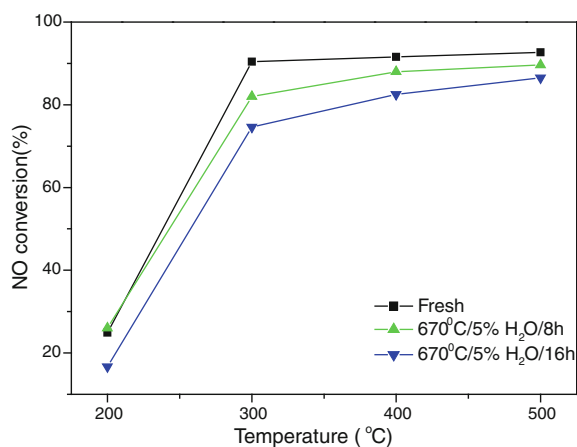
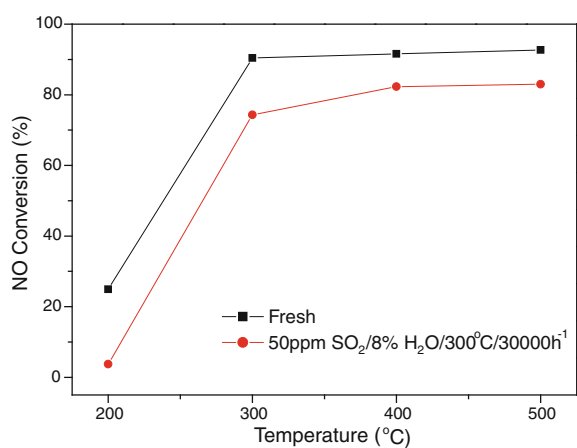
catalysts [11]. In the present work, Pt and Rh respectively supported on the Ba/CeO<sub>2</sub>-ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which may improve the interaction between NM, storage component and support, resulted in the superior NSR activity. The results show that Pt/BaO/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> + Rh/AC catalyst has superior NSR activity (as shown in Fig. 5).

### 3.4 Hydrothermal Stability

Thermal degradation of NSR catalysts is primarily caused by high temperature desulfation treatment. Furthermore, during a rich-burn cycle, the oxidation of hydrocarbon, CO and H<sub>2</sub>, generates heat at the catalyst surface and results in thermal degradation as well [3, 6]. Coarsening of the platinum particles and the loss of surface area of the NOx storage materials are two of the factors that can contribute to the loss of NOx storage capacity after thermal aging. The NSR performances of the hydrothermal aged catalysts are showed in Fig. 6. Aged catalysts exhibit different extents of NOx storage capacity decline due to the consumption of BaCO<sub>3</sub> and the collapse of physical texture of support oxides at different levels. However, CZ solid solutions are well known for their improved redox activities and thermal stability [12]. Furthermore, Rhodium containing catalysts showed relatively little loss of activity upon hydrothermal aging [9, 13]. So best NSR performance and thermal stability was observed with bimetallic catalysts where the noble metals were separated.

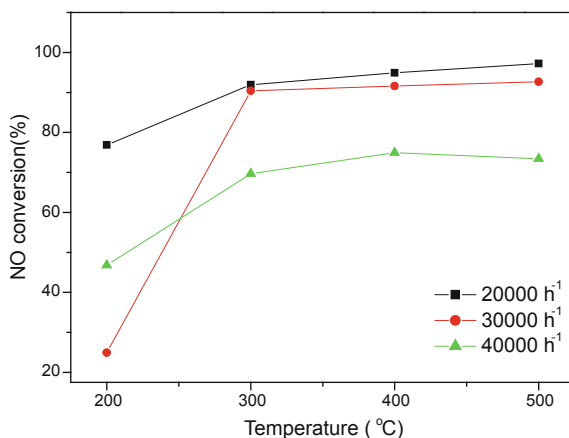
### 3.5 Sulfur Tolerance

Sulfur typically present in the fuel and lubricant oils is oxidized to SO<sub>2</sub> during combustion. The SO<sub>2</sub> in the exhaust gas can adsorb on the catalyst and poison it. As concerns the noble metal, SO<sub>2</sub> can have negative as well as positive influence

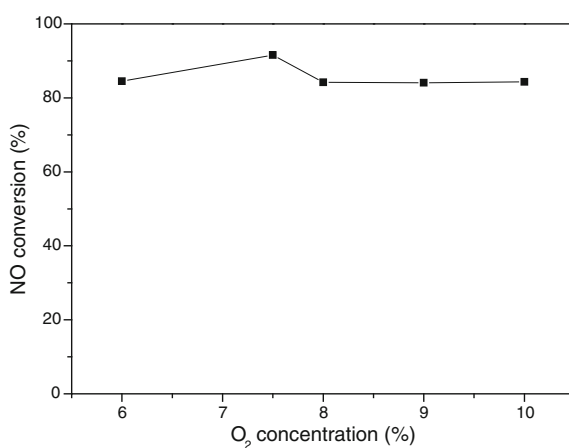
**Fig. 6** Influence of on NSR activity**Fig. 7** Influence of sulphur on NSR activity

on the catalyst's oxidation activity. In contrast to Pt, for Rh no loss of NO reduction activity was observed in the presence of SO<sub>2</sub>. Furthermore Rh is a highly active NO reduction catalyst that enhances the regeneration of Ba-nitrates [9]. According to Corbos et al. [14], the Pt/Ba/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts showed better sulfur resistance than Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalysts. Meanwhile, the sulfates elimination under desulfation conditions was more efficient on Pt/Ba/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> than on the Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst. The Influence of sulfur on NSR activity is shown in Fig. 7. The results show that the Pt/BaO/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> + Rh/AC catalyst has superior sulfur tolerance.

**Fig. 8** Influence of space velocity on NSR activity



**Fig. 9** Influence of O<sub>2</sub> concentration on NSR activity at 400 °C



### 3.6 Influence of Different Operating Conditions

The performance of an automotive catalytic converter is strongly influenced by the space velocity of the exhaust gases [15–18]. The catalyst conversion performance decreases with increasing space velocity and can be severely deteriorated when space velocity is increased beyond certain values. At higher space velocities, the exhaust gases passing through the catalyst may not have sufficient residence time for the catalytic reactions resulting in a reduced conversion performance. Low space velocities, on the other hand, yield excellent conversion performance, but may require low gaseous flow rates through the engine or the use of larger size catalysts. Figure 8 shows a comparison of the influence of different space velocities on the NSR performance. Obviously a higher space velocity (GHSV) reduces the conversion efficiency, because of short residence time.



**Fig. 10** Influence of lean-rich time on NSR activity at 400 °C

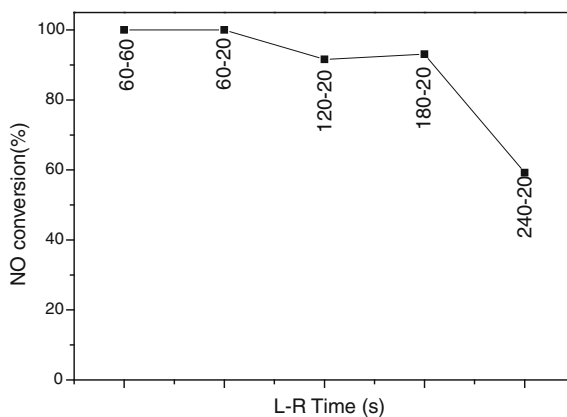


Figure 9 shows the influence of oxygen concentration in the lean phase on the NSR activity at 400 °C. These plots prove the zero-order kinetics with respect to oxygen for O<sub>2</sub> feed concentrations in the investigated range.

The lean pulse duration is varied keeping the rich phase duration constant at 20 s and the feed CO at 7.5 % and the temperature at 400 °C. It can be seen from Fig. 10 that NO conversion is a monotonically decreasing function of lean pulse duration. As we known, during the lean phase Pt sites are covered with oxygen. When the CO is injected it reacts with oxygen, enabling the subsequent adsorption and reduction of NO<sub>2</sub>. If the lean pulse is too long in duration, not all of the NO<sub>2</sub> is reduced and the NO<sub>2</sub> conversion is incomplete. As the lean pulse duration is decreased, the additional CO consumes more oxygen, freeing up sites for NO<sub>2</sub> adsorption and reduction. This leads to an increase in NO<sub>2</sub> conversion.

## 4 Conclusion

The Pt/BaO/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> + Rh/AC catalyst shows superior NSR activity, thermal stability, sulfur tolerance and adaptability for different operating conditions.

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